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[54] **PROCESS OF PREPARING NOBLE METAL**
MATERIALS HAVING IMPROVED HIGH
TEMPERATURE STRENGTH PROPERTIES
15 Claims, 1 Drawing Fig.

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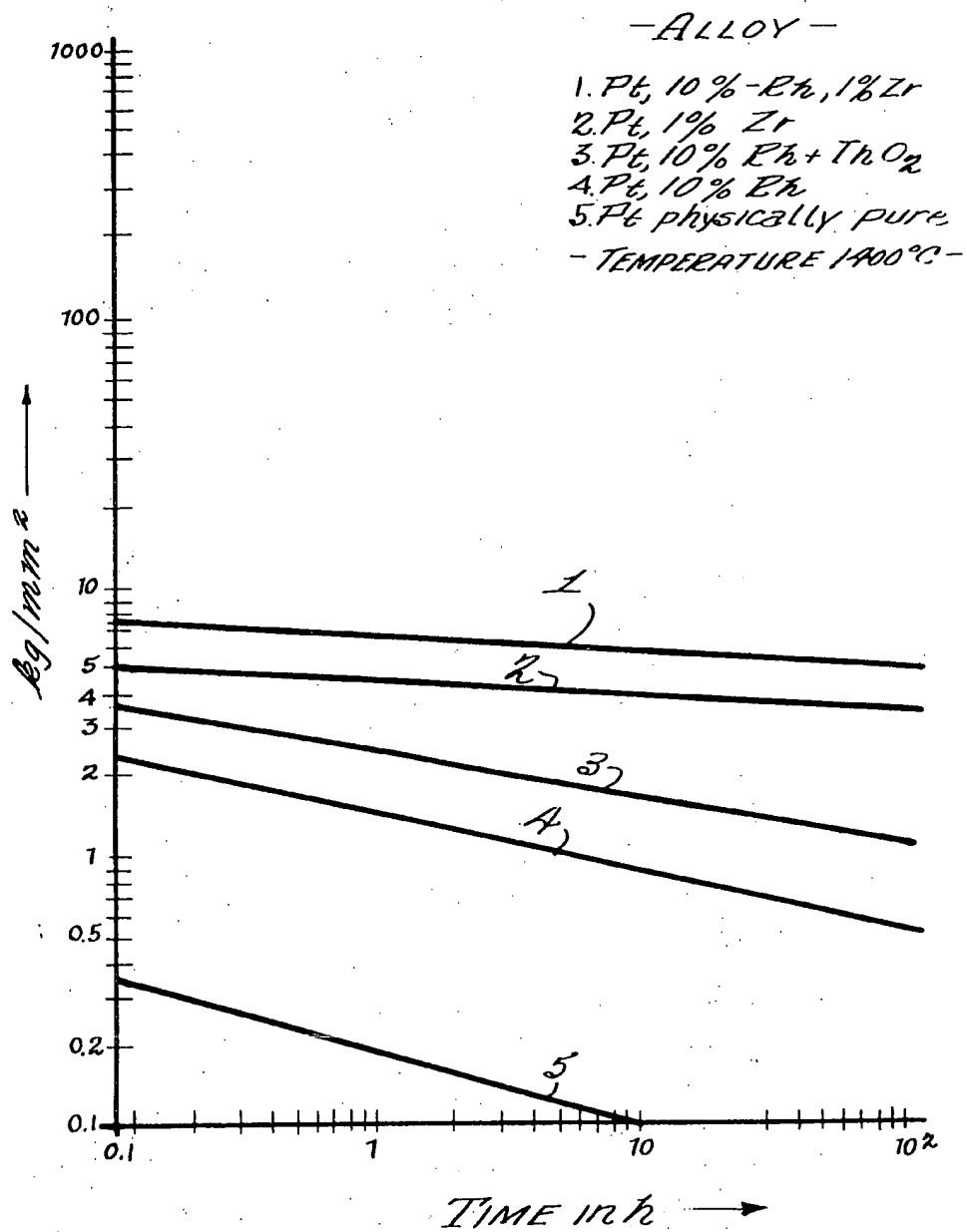
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ABSTRACT: The high temperature strength properties of noble metals, particularly platinum are improved by adding an element having an affinity for oxygen, preferably zirconium, and heating either (1) at 800° to 1,200° C. or (2) stepwise heating at 300° to 800° C. followed by heating at 800° to 1,400° C.



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PROCESS OF PREPARING NOBLE METAL MATERIALS HAVING IMPROVED HIGH TEMPERATURE STRENGTH PROPERTIES

Platinum and platinum alloys find extensive use in cases where high resistance to corrosion or to oxidation at high temperatures is important. A disadvantage of platinum and its alloys with other noble metals is visible in their relatively poor strength at high temperatures. An alloy with non noble metals which can bring about a strong increase in strength under certain conditions fails, however, as soon as it is placed in an oxidizing atmosphere at high temperatures.

Consequently there is not a lack of experiments for hardening and strengthening platinum by the addition of materials inert in an oxidizing atmosphere, e.g., high melting oxides. A large number of suggestions of processes to produce dispersion strengthened platinum have already been made.

For example it has been suggested to mechanically mix fine grained platinum powder with fine grained high melting oxide powder and to work up this mixture by powder metallurgy. It is also known to carry out the preparation of hardened pieces by simultaneous precipitation from salt solutions through the vaporation of solution containing both components or by spraying such solutions in a flame. Further processes include surface oxidation of alloy powder or common deposition from solution through a combination of galvanic separation and electrophoresis.

All of the processes have the disadvantage that the execution is relatively troublesome and expensive. The reproducibility of the properties moreover is not very good and the improvement of the properties compared to materials without additives is relatively small.

For platinum alloys there has also been proposed the process of internal oxidation. This internal oxidation of alloys of noble metals with addition of relatively small amounts of such metals whose oxides have a high energy of formation has the advantage that it leads by appropriately conducted experiments to uniform and fine separations of the oxide in the matrix. A fine separation (particle diameter below 1 μ), however, is necessary to produce an essentially dispersion hardening effect. Prerequisite for the internal oxidation of an alloy is a not too small solubility of oxygen in the matrix metal and as great as possible difference in the oxygen affinity of both members of the alloy. In addition the diffusion rate of oxygen in the matrix must be greater than that of the constituent to be alloyed and the solubility of the oxide formed in the matrix should be as small as possible.

While, for example, silver fulfills all of these conditions, platinum lacks as the matrix the required relatively high solubility of oxygen. It is so small that in the known processes no true internal oxidation occurs, but in general only an outer scale formation occurs, whereby along the grain boundaries in the interior of the material oxide separation also can occur on account of the easily diffusing oxygen at that place.

Surprisingly it has now been found that alloys of one or more of platinum and platinum metals, for example rhodium, or gold, with elements having an affinity for oxygen, especially zirconium, are capable of internal oxidation, i.e., they become oxidized not only on the grain boundaries but also in the interior of the grain, if the initial material is subjected to an annealing at a temperature between 800° and 1,200° C. for over 5 hours in air or an oxygen containing atmosphere. The maximum time of annealing is not critical but normally is not over 500 hours.

Preferably there is used as the initial material a powder of the alloy, however, it is also possible to subject shaped parts or semifinished products directly to a corresponding treatment.

Above 1,200° C. there occurs practically only grain boundary oxidation whilst below 800° C. the oxidation is so slow that an oxidation depth of about 100 μ occurs only after an annealing time of over 1000 hours.

It is especially advantageous to carry out the heat treatment in two steps. In the first step an annealing treatment at a temperature between 300° and 800° C. is carried out for 5 to 500 hours and in the second step an oxidation treatment at a tem-

perature between 800° and 1,400° C. is carried out for 0.5 to 50 hours. By this especially preferred process it is possible in the two steps to go up to 1,400° C. with the oxidation treatment and thereby shorten the oxidation time, e.g. to 0.5 hours, since after a preceding annealing treatment between 300° and 800° C. no grain boundary oxidation takes place between 1,200° and 1,400° C., in contrast to nonpreannealed alloys. Hence it is possible, for example with an alloy of platinum with 1 percent of zirconium or with alloys of platinum together with other noble metals, and for example, 1 percent zirconium to attain still higher hardnesses through internal oxidation. These high hardnesses also decrease only immaterially after long annealing at 1,400° C. Additionally alloys of this type exhibit very good time to rupture properties at high temperatures. Thus, for example for a time to rupture of 1,000 hours at 1,400° C. there is an increased resistance to break by a factor of 20 compared to an alloy of platinum with 10 percent rhodium without oxide inside the grain and also as compared to the best of the known dispersion strengthened platinum alloys there is still almost a 10 times higher value. With stresses with which the platinum 10 percent rhodium alloy without oxide inside the grain breaks after 1 hour at 1,400° C. materials according to the invention will practically never break at such temperature. The stress tolerated of the best of the previously known dispersion strengthened platinum alloys at a temperature of 1,400° C. for 1 hour the alloys of the invention endure up to 1 million hours (by extrapolation).

The single FIGURE of the drawings is a graph of tensile strength of platinum and platinum alloys against time at 1,400° C.

The process according to the invention is not limited to platinum and its alloys with other noble metals. In the same manner palladium and palladium alloys can be dispersion strengthened with other noble metals. There can also be employed other metals and alloys of such metals of the platinum group including rhodium, ruthenium, iridium and osmium. Even gold and its alloys is hardenable by the method of the invention, although in this case the described effect is not quite as high as with the platinum metals.

When platinum is alloyed with palladium, rhodium, gold or other noble metal the content of palladium, rhodium, or the like can be 1 to 49 percent.

As additives to the named noble metal alloys there are suited not only zirconium but also other elements whose oxides exhibit a high heat of formation. Examples of such elements are aluminum, beryllium, titanium, hafnium, tantalum, and the like. As previously set forth zirconium is preferred. The content of the added metal can be between 0.1 and 5 percent, preferably between 0.5 and 2 percent.

A shortening of the annealing time can be accomplished by oxidation under elevated oxygen pressure.

The internal oxidation of alloys according to the invention can also take place directly on sheets or wires as well as on powders of the corresponding alloys in order to shorten the oxidation time. In such case it is immaterial how the powder is produced, for example by spraying a melt, by flame spraying a wire, or by size reduction through the taking off of shavings. When powders are employed preferably the grain size is 5 to 500 μ .

The following illustrative examples are presented for a better understanding of the invention.

EXAMPLE I

Alloys of (a) platinum with 1 percent zirconium, (b) platinum with 9.5 percent palladium and 1 percent zirconium and (c) platinum with 10 percent rhodium and 1 percent zirconium were produced by fusion and filed to fine powders with a grain size between about 100 and 300 μ . These powders were kept in air at 750° C. for 136 hours and following internally oxidized for 15 hours at 1,000° C. in air. After this treatment the powder was cold pressed with 4 tons per cm^2 , sintered in air for 1 hour at 1,400° C. and hot rolled at 1,200°

C. to sheets of 0.5 mm. thickness. After that the sheets in the above named series showed the following hardness values (HV 0.5) in kg./mm.² at room temperature (a) 230, (b) 228 and (c) 255. Annealing of 1 hour at 1,400° C. in air resulted only in a falling of the hardness to (a) 205, (b) 207 and (c) 238 kg./mm.². A further annealing of 500 hours in air at 1,400° C. resulted in no further decrease in hardness. The pure alloys without a zirconium oxide portion after a corresponding production and treatment showed only the following hardness values, (a) 50, (b) 60 and (c) 80 kg./mm.². Thus essentially permanent increase in hardness occurs.

EXAMPLE 2

A cast ingot of each of the alloys containing zirconium identified in example 1 was cut on a lathe. The turnings obtained were treated in the same manner as in example 1 and worked to wires of 1 mm. diameter by hot rolling at 1,200° C. and finally with cold drawing. After an annealing for 1 hour at 1,400° C. in air they had the following tensile strengths at room temperature, (a) Pt, 1% Zr, 48 kg./mm.², (b) Pt, 9.5% Pd, 1% Zr, 45 kg./mm.² and (c) Pt, 10% Rh, 1% Zr 65 kg./mm.². The tensile strength of the materials without the addition of the ZrO₂ portion amounted to (in the same sequence) (a) 15, (b) 20 and (c) 30 kg./mm.². In comparison the literature gives a value for ThO₂ hardened platinum with 10 percent rhodium. After annealing at 1,400° C. for 1 hour the strength is 36 kg./mm.². This value also lies considerably lower than that for the interiorly oxidized platinum produced according to the invention, since an alloy of platinum with 10 percent rhodium according to the process of the invention shows an approximately double tensile strength.

EXAMPLE 3

The alloys of platinum with 1 percent zirconium and platinum with 10 percent rhodium and 1 percent zirconium were melted, homogenized for 2 hours at 1,100° C. in a vacuum of 10⁻⁷ torr and processed by filling to a powder. The powder was kept at 700° C. in air for 100 hours followed by annealing with oxidation for 10 hours at 1,000° C. in air. Rods were compressed from these materials, sintered and hot and cold worked to wires of 1 mm. diameter. Time to rupture tests at 1,400° C. in air were carried out with these materials. The results are shown in the single figure of the drawings in which both the time and tensile strength values are measured on logarithmic scales. The straight line graphs are as follows:

1. platinum alloyed with 10 percent rhodium and 1 percent zirconium treated according to the invention,
2. platinum with 1 percent zirconium treated according to the invention,
3. The values obtained from the literature for a ThO₂ hardened platinum alloyed with 10 percent rhodium (produced through simultaneous precipitation),
4. platinum alloyed with 10 percent rhodium without an additive, and
5. physically pure platinum.

From the drawing it is seen that the alloys according to the invention are superior to all the comparison materials in two respects. Firstly for a required time to rupture the stress tolerated is generally higher than with the comparison materials of which (3) gives the best previously known values. Secondly the slope of the straight line for the samples according to the invention is substantially smaller than that for the comparison materials. This means that the alloys of the invention behave better in comparison to the other samples, the longer the time required to rupture.

Thus the 100 hour time strength for alloys (1) and (2) of the invention are 5.2 and 3.6 kg./mm.² respectively, for (3) only 1.1 kg./mm.², for (4) only 0.54 kg./mm.² while (5) loses all of its strength long before the 100 hours is up (actually at less than 10 hours). The improvement of alloys (1) and (2) of the invention in comparison with (4) is about tenfold and sevenfold respectively and in comparison to (3) is about fivefold

and threefold respectively. By extrapolation to 100,000 hours the numerical values (in the same sequence) are (1) 3.5, (2) 2.8, (3) 0.32 and (4) 0.115 kg./cm.². This is an improvement of (1) and (2) in comparison with (4) of over 30 times and 24 times respectively and in comparison with (3) of 11 times and 9 times respectively.

EXAMPLE 4

A sheet of 1 mm. thickness of an alloy of platinum with 1 percent zirconium was annealed at 1,000° C. in air. After that the sheet showed the following hardness values:

Treatment 20 hours

HV 106-114 kg./mm.² (Vickers hardness)

Treatment 110 hours

HV 103-106 kg./mm.².

A sheet of unalloyed platinum showed after the same annealing process a hardness value of 50 kg./mm.².

EXAMPLE 5

A filing powder of an alloy of platinum with 1 percent zirconium was kept at 700° C. a) in air, b) in oxygen at 1 at, c) in oxygen at 5 at for 50 hours followed by annealing with oxidation for 16 hours at 1,000° C. in air. The hardness was a) 150 kg./mm.², b) 185 kg./mm.² and c) 195 kg./mm.².

EXAMPLE 6

A filing powder of alloys of platinum with 1 percent aluminum and of platinum with 1 percent tantalum was kept at 700° C. for 142 hours in air, followed by annealing of oxidation for 16 hours at 1,000° C. in air. The hardness was for Pt/Al 160 kg./mm.² and for Pt/Ta 150 kg./mm.². The same nonoxidized alloys showed a hardness of 95 and — 110 kg./mm.².

What is claimed is:

1. A process of preparing an internally oxidized dispersion hardened noble metal selected from the group consisting of platinum metals and fold and mixtures thereof alloyed with an element having an affinity for oxygen selected from the group consisting of zirconium, aluminum, beryllium, titanium, hafnium, and tantalum comprising subjecting the initial material to a stepwise treatment including a pretreatment at 300°-800° C. followed by treatment with an oxygen containing atmosphere at a temperature of 800° C. to 1400° C. for a time sufficient to improve the high temperature strength of the noble metal.

2. A process according to claim 1 wherein the annealing treatment is in an oxygen containing atmosphere at 800° to 1200° C. for at least 5 hours and the element having an affinity for oxygen is present in an amount of 0.1 to 5 percent.

3. A process according to claim 2 wherein said element is zirconium.

4. A process according to claim 3 wherein the noble metal is predominantly platinum.

5. A process according to claim 2 wherein the zirconium is between 0.5 and 2.

6. A process according to claim 5 wherein the noble metal is a platinum-rhodium alloy containing 1 to 49 percent rhodium.

7. A process according to claim 6 wherein the rhodium is 10 percent and the zirconium is between 0.5 and 2 percent.

8. A process according to claim 7 wherein the noble metal is a platinum-palladium alloy containing 1 to —49 percent palladium.

9. A process according to claim 1 where the element having an affinity for oxygen is present in an amount of 0.1 to 5 percent.

10. A process according to claim 9 wherein said element is zirconium.

11. A process according to claim 10 wherein the noble metal is predominantly platinum.

12. A process according to claim 11 wherein the zirconium is between 0.5 and 2 percent.

13. A process according to claim 12 wherein the noble metal is a platinum-rhodium alloy containing 1 to 49 percent rhodium.

14. A process according to claim 1 wherein the noble metal is treated in powdered form.

15. A process of preparing the product of claim 1 wherein the oxygen containing atmosphere is air.

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